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Mechanical Properties and Structure of Novel Polymer Blends and Composites Fabricated by Reactive and High-shear Rotational Processing

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Abstract

Various polymer alloys have been examined to achieve performance beyond that of single polymers. Polyamide 6 (PA6) has extraordinary mechanical properties, impact absorbability, and high heat resistance necessary for exterior and interior automotive applications. Nevertheless, some materials and their combinations can exhibit inferior physical properties. This paper describes a novel polymer blend with PA6, fabricated using high-shear rotational processing. Modulated differential scanning calorimetry (M-DSC), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) elucidated thermal properties and morphologies of PA6 blends. Tensile and Izod tests revealed their mechanical properties. Results show that novel PA6 blends are useful for automotive applications.

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Keywords: Polyamide blends and composites, Polyamide 6 (PA6), High-shear rotational process, Mechanical properties, Morphology

1. Introduction

High performance and multi-functionalization of plastic products with characteristics needed for polymer materials have become widely explored. Polymer alloys with various polymer materials have been studied to assess

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their performance, which transcends that of single polymers. Furthermore, nanoalloys having various characteristics have been proposed. Their reported mechanical properties have been improved drastically [1]. Nevertheless, depending on the selected materials and their combinations, they can be immiscible. Sometimes, their physical properties become worse. Therefore, considerable effort has been taken to develop new materials. Polyamide 6 (PA6) has excellent mechanical properties, impact absorbability, and high heat resistance, which are all required for their use as exterior and interior automotive materials. Accordingly, polymer blends and composites using PA6 have been studied. However, optimizing the balance of rigidity and ductility of PA6 blends persists as a main research topic. In this study, high shear processing technology of a novel fabrication process is used with a screw with a return hole. Moreover, finely dispersed immiscible combinations of PA6 and PP have been done with micrometer and nanometer order. Then the effects on the microstructures and mechanical properties were evaluated.

2. Experimental

2.1. Samples

Polyamide 6 (PA6) was used (T840; Toyobo Co. Ltd.) with polypropylene (PP, J108M; Prime Polymer Co. Ltd.) was used. The compatibilizer was maleic anhydride-modified PP (PP-g-MAH, Yumex 1010; Sanyo Chemical Industries Ltd.). The PA6 and PP blending ratio was 7: 3 (wt). The compatibilizer additive amount was 5 wt%. Table 1 presents the sample characteristics.

Table 1. Characteristics of sample.

Materials		MFR at 230℃ (g/10 min)	T_g (℃)	T_m (℃)	Actual producer
PA6	T840	80	50	220	TOYOBO CO., LTD.
PP	J108M	45	0	165	Prime Polymer Co., Ltd.
PP-g-MAH	Yumex 1010	-	-	148	Sanyo Chemical Industries, Ltd.

2.2. High-shear rotational processing overview and mixing conditions

We used a high-shear rotational processing machine (NHS2-28; Niigata Machine Techno Co., Ltd.) for melt mixing of the PA6/PP blend. A schematic illustration of the high-shear processing machine screw is presented in Fig. 1. The high-shear processing machine is used for this novel fabrication process with mixing by high-speed screw rotation (max. 3000 min^{-1}) and extensional flow [2] passing through the return hole of the screw [3, 4].

We conducted melt mixing at 230°C. The return hole diameter of the screw was 0.5 mm. Screw rotation speeds were 500, 1500, and 3000 min^{-1}. Mixing times were 10 s and 30 s. After high-shear processing, dumbbell specimens were molded using a micro-injection molding machine (ELJECT AU3E-s; Nissei Plastic Industrial Co. Ltd.).

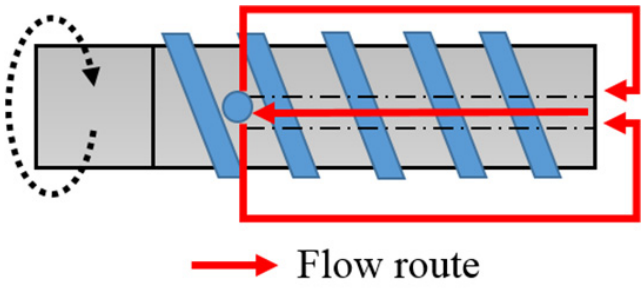

Fig .1 Schematic illustration for High-shear processing machine screw

2.3. Thermal properties

The melting temperature (T_m) and crystallinity (X_c) of PA6, PP, and PA6/PP alloy material were measured using a modulated differential scanning calorimeter (M-DSC, Q100; TA Instruments) under nitrogen flow. The rate of temperature increase was 5°C/min. Actually, X_c is known to be calculable from the crystal fusion heat determined and ideal crystal fusion heat determined using M-DSC. For ideal determined crystal fusion heat, we used PA6 (230 J/g) and PP (207 J/g) [6].

2.4. Observation of internal structure and morphology

We observed the internal structure and morphology after high-shear processing. After freeze fracture, the fracture surface was deposited using Pt-Pd. The micro-order structure was observed using a scanning electron microscope (SEM, TM-1000; Hitachi High-Technologies Corp.). The nano-order structure was observed using a transmission electron microscope (TEM, JEM2100F; JEOL Ltd.). The TEM observation sample was obtained after staining by RuO_4 and OsO_4, yielding ultra-thin sections using an ultramicrotome (ULTRACUT-UCT; Leica Microsystems).

2.5. Mechanical properties

Tensile tests of the mechanical properties evaluation were measured (Strograph VGS-E01; Toyo Seiki Seisaku-Sho Ltd.). Tensile tests were conducted at a rate of 5 mm/min at 25°C.

Izod impact tests were done using a digital impact tester (DG-1B; Toyo Seiki Seisaku-Sho Ltd.). Izod impact test specimens were mounted at a notch depth of 0.5 mm. Izod impact tests were conducted at 25°C, with 1.0 J hammer weight at a 150° initial angle.

3. Results and discussion

3.1. M-DSC measurements

The results of M-DSC measurement of neat PA6, neat PP, and PA6/PP alloy, and neat PA6, neat PP, and PA6/PP/PP-g-MAH alloy are shown respectively in Figs. 2(a) and 2(b). High shear processing conditions of PA6/PP alloy and PA6/PP/PP-g-MAH alloy are 500 min^{-1}/10 s and 3000 min^{-1}/30 s. Test results confirmed that the T_m peak temperature of PA6 and PP in PA6/PP alloy and PA6/PP/PP-g-MAH alloy were shifted to the low temperature side by high shear processing. The shift amount increases with increased screw rotation speed. In addition, the shift amount was found to be increased by the addition of PP-g-MAH. Figure 3 presents effects of the crystallinity X_c by high shear processing conditions of PA6/PP alloy and PA6/PP/PP-g-MAH alloy. Results verified that crystallinity of PP in PA6/PP alloy was decreased by an increase of the screw rotation speed. Additionally, crystallinity was decreased by the addition of PP-g-MA. These results suggest that the PP domains were dispersed similarly to islands in the PA6 matrix. They were finely distributed by high shear processing and the addition of PP-g-MAH. In contrast, the crystallinity of PA6 was increased by the increase of the screw rotation speed. Increased crystallinity might occur as a result of the promoted crystallization, in strong shear and effects of stretching molecular chains with high shear processing.

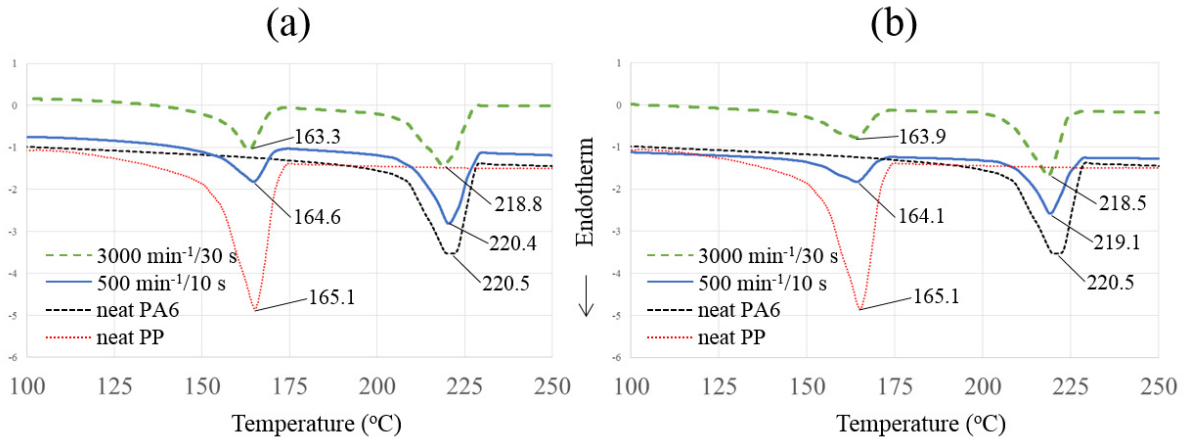

Fig .2 M-DSC measurement results of (a) neat PA6, neat PP, PA6/PP alloy (500 min^{-1}/10 s), PA6/PP alloy (3000 min^{-1}/30 s) and (b) neat PA6, neat PP, PA6/PP/PP-g-MAH alloy (500 min^{-1}/10 s), PA6/PP/PP-g-MAH alloy (3000 min^{-1}/30 s).

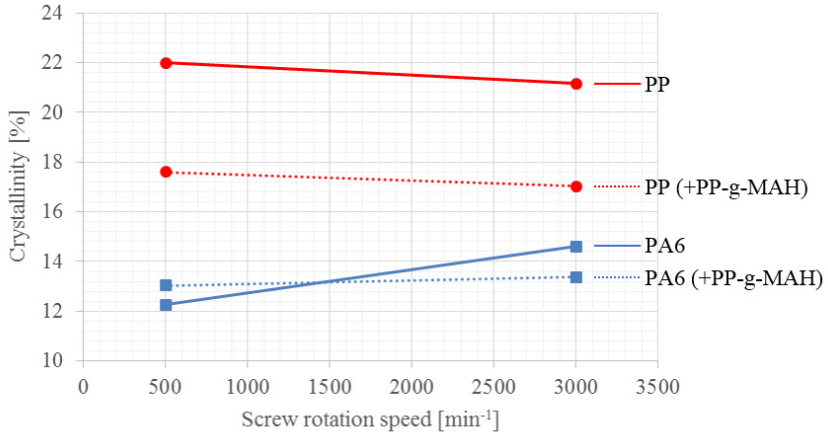

Fig .3 Effect of screw rotation speeds on the crystallinity of PA6/PP alloy and PA6/PP/PP-g-MAH alloy.

3.2. SEM and TEM

SEM images of PA6/PP alloy and PA6/PP/PP-g-MAH alloy are portrayed in Fig. 4. The PP domain diameters in PA6/PP alloy were, respectively, about 40, 30, and 10 μm in the high shear process conditions of (a) 500 min^{-1}/30 s, (b) 1500 min^{-1}/30 s, and (c) 3000 min^{-1}/30 s. The PP domain diameter decreased with increased screw rotation speed, but it did not engender nano-dispersion. The PP domain diameters in PA6/PP/PP-g-MAH alloy were less than 2 μm for the high shear process conditions of (d) 500 min^{-1}/30 s, (e) 1500 min^{-1}/30 s and (f) 3000 min^{-1}/30 s. Particularly under the condition of (f) 3000 min^{-1}/30 s, the PP domain diameter was dispersed to 1 μm or less. The SEM observation results confirmed the promotion of dispersed PP by addition of PP-g-MAH and the increase of screw rotation speed with high shear processing.

The morphology and internal structure of nano-order were observed using TEM. Some TEM images of PA6/PP alloy and PA6/PP/PP-g-MAH alloy are presented in Fig. 5. The PP domain diameters in PA6/PP alloy fabricated under conditions of 3000 min^{-1}/30 s were about 3–10 μm. In addition, the minimum diameters were reduced to approximately 200 nm. The PP domain diameter in PA6/PP/PP-g-MAH alloy fabricated under condition of 3000 min^{-1}/30 s was 1 μm or less. Furthermore, minimum diameters were reduced to 10 nm. The TEM observation results confirmed the promotion of dispersed of PP by high shear processing. In addition, for the PP domain diameter, nano-dispersion proceeds to a greater degree while stabilized by the addition of PP-g-MAH.

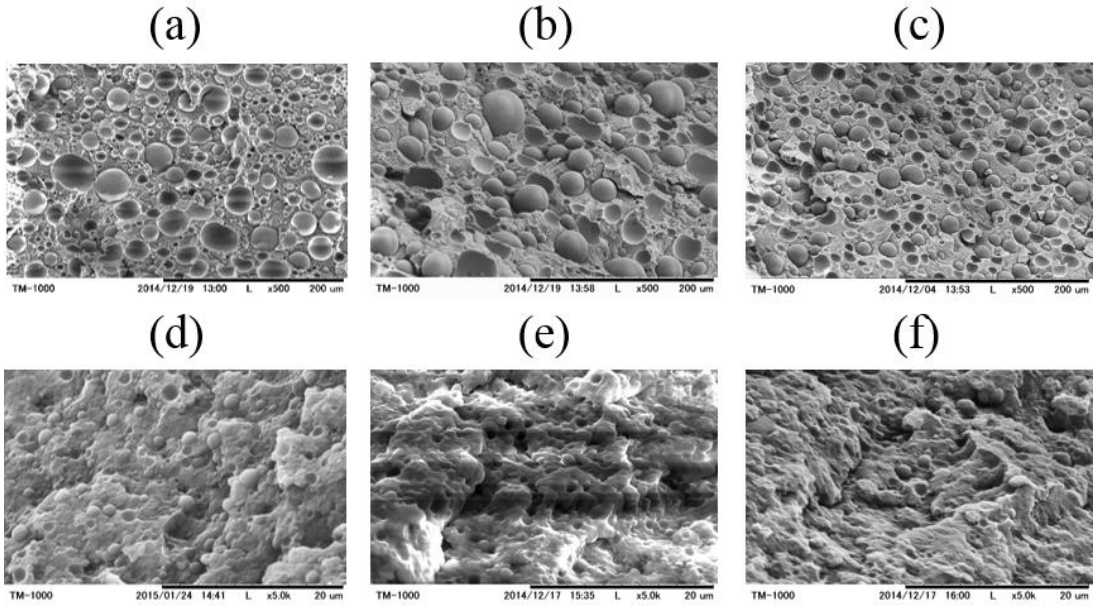

Fig .4 SEM image of PA6/PP alloy ; (a) 500 min^{-1}/30 s, (b) 1500 min^{-1}/30 s, (c) 3000 min^{-1}/30 s.
PA6/PP/PP-g-MAH alloy ; (d) 500 min^{-1}/30 s, (e) 1500 min^{-1}/30 s, (f) 3000 min^{-1}/30 s.

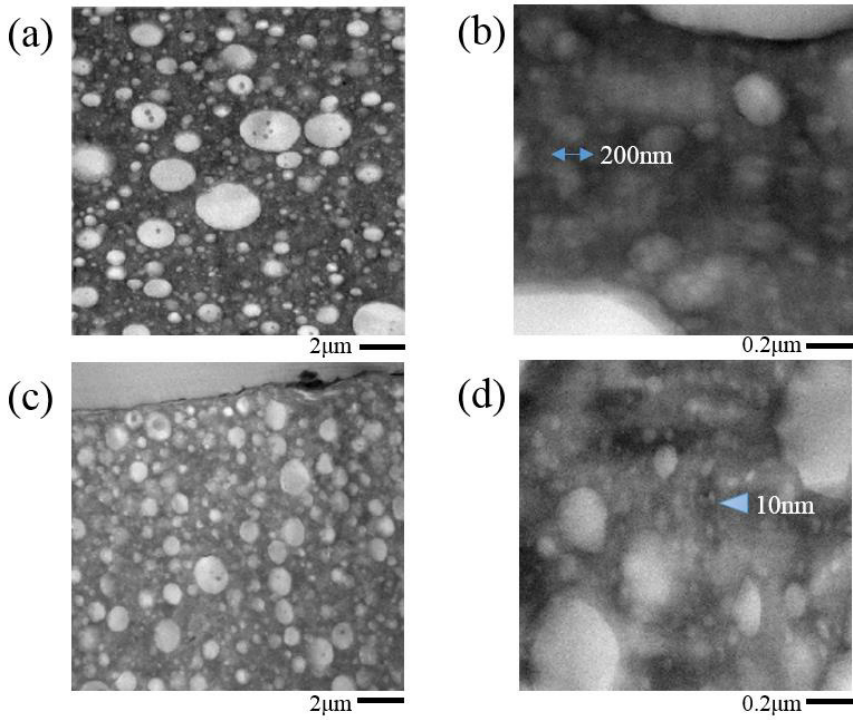

Fig .5 TEM images of PA6/PP alloy (3000 min^{-1}/30 s) : (a) low magnification, (b) high magnification.
PA6/PP/PP-g-MAH alloy (3000 min^{-1}/30 s) : (c) low magnification, (d) high magnification.

3.3. Mechanical properties

3.3.1 Tensile tests

The stress–strain curves in tensile tests are depicted in Fig. 6. Table 2 presents the modulus and the yield strength. From Fig. 6, it is apparent that PA6/PP alloy fabricated for 500 min broke at very low strain (= 0.2). Furthermore, the modulus and yield strength were lower than those of neat PA6 because the coarse size PP (40 μm) domain remained without dispersion. Results demonstrate that stress concentration occurred and led to ease of breakage. However, for PA6/PP/PP-g-MAH alloy fabricated under the condition of 500 min^{-1}/10 s, the breaking strain, modulus and yield strength were higher than those of neat PA6. The adhesion of the PA6/PP interface was increased because most of the PP domain was finely dispersed to 2 μm or less and because of the addition of PP-g-MAH. Consequently, the stress dispersed; uniform deformation occurred. In contrast, PA6/PP/PP-g-MAH alloy fabricated under condition of 3000 min^{-1}/30 s showed considerably lower breaking strain and yield strength than that of neat PA6, probably because the molecular weight was reduced by increasing the high-shear rotation.

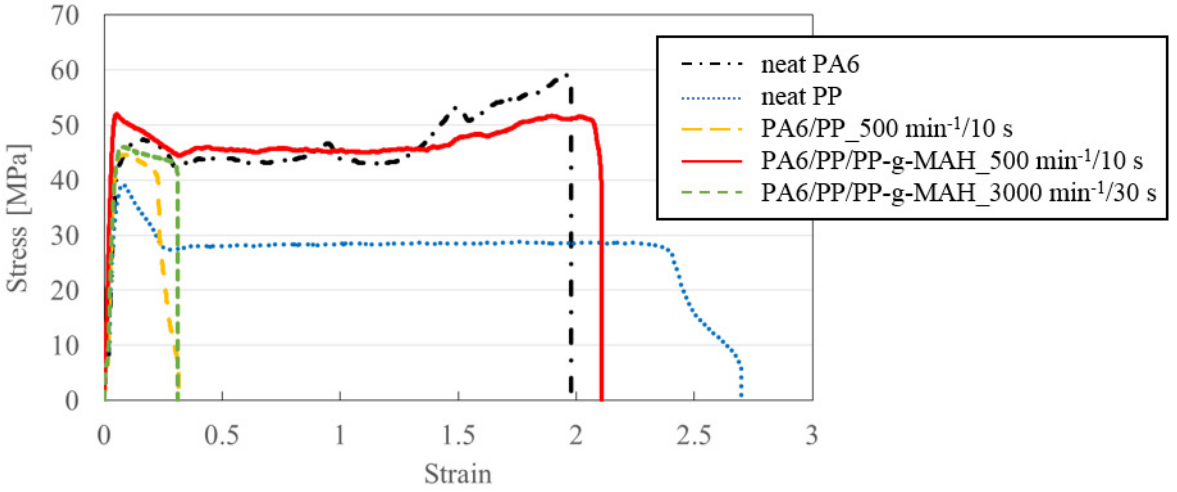

Fig .6 Stress-strain curves of neat PA6, neat PP, PA6/PP alloy (500 min^{-1}/10 s), PA6/PP/PP-g-MAH alloy (500 min^{-1}/10 s) and PA6/PP/PP-g-MAH alloy (3000 min^{-1}/30 s).

Table 2. Modulus and Yield strength of samples.

	PA6	PP	PA6/PP alloy (500 min^{-1}/10 s)	PA6/PP/PP-g-MAH alloy (500 min^{-1}/10 s)	PA6/PP/PP-g-MAH alloy (3000 min^{-1}/30 s)
Modulus [GPa]	1.4	0.7	1.1	1.4	1.5
Yield strength [MPa]	48	39	44	52	46

3.3.2. Izod impact tests

The Izod impact test results are portrayed in Fig. 7. The impact value *ak* of PA6/PP alloy fabricated under conditions of 500 min^{-1}/10 s is 6.6 KJ/m^2, which was lower than that of neat PA6. Tensile test results show weak properties against impact because the PP dispersion was not progressing. However, the impact value *ak* of PA6/PP/PP-g-MAH alloy fabricated under 500 min^{-1}/10 s was 10.9 KJ/m^2, and higher than neat PA6. Results show that PP, despite accounting for 30 wt%, can exhibit higher toughness than PA6 by nano–micro dispersion of PP.

However, the impact value *ak* of PA6/PP/PP-g-MAH alloy fabricated under conditions of 3000 min^{-1}/30 s was 5.7 KJ/m^2, which was lower than that of neat PA6. Although the dispersibility was improved by high shear processing, the molecular weight was reduced by kneading of intense shear and the long duration. Thereby, toughness is reduced.

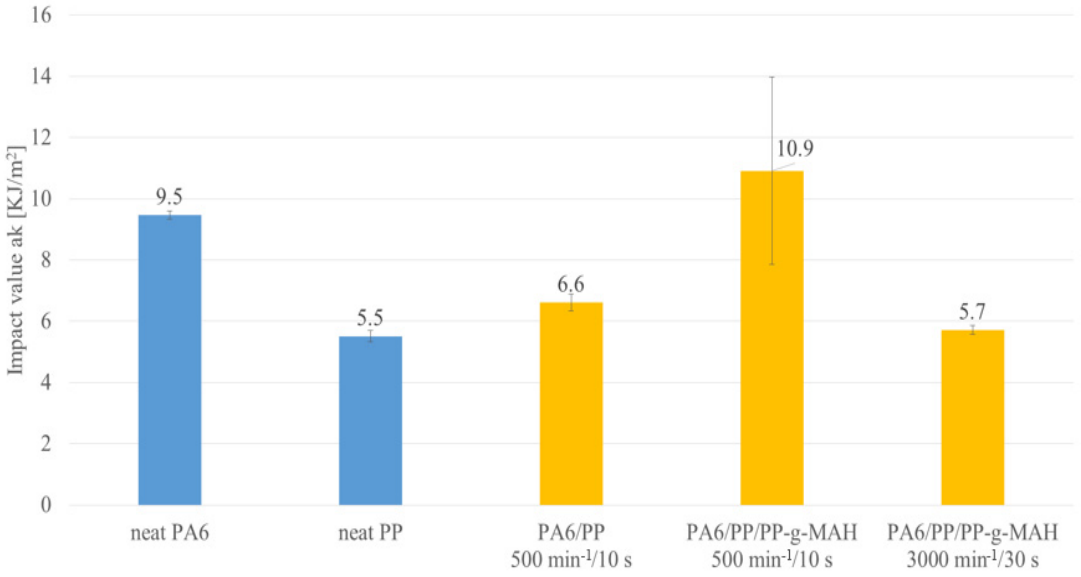

Fig .7 Impact energy *ak* of neat PA6, neat PP, PA6/PP alloy (500 min^{-1}/10 s), PA6/PP/PP-g-MAH alloy (500 min^{-1}/10 s) and PA6/PP/PP-g-MAH alloy (3000 min^{-1}/30 s)

4. Conclusion

We fabricated a novel PA6 nano-alloy using melt mixing with high shear processing. The M-DSC measurement results show that its crystallinity was changed by the screw rotation speed. Furthermore, the crystallinity X_c of PP was reduced during high shear processing. However, X_c of PA6 was found to increase with the screw rotation speed. These results suggest that the PP domains are dispersed like islands in the PA matrix. They are finely distributed by high shear processing and the addition of PP-g-MAH.

We observed the internal structure and morphology after high-shear processing. The PP domain diameter in PA6/PP/PP-g-MAH alloy was 1 μm or less. The minimum ones were as small as 10 nm. Accordingly, results show the promotion of dispersed PP by addition of PP-g-MAH and the increase of the screw rotation speed with high shear processing.

We evaluated the mechanical properties of the novel PA6 nano-alloy fabricated by high shear processing. Results show that PP, despite accounting for 30 wt%, exhibits superior toughness to that of PA6 by nano–micro dispersion PP. Unfortunately, the strain at break and yield stresses was reduced by increasing screw rotation: the molecular weight can be reduced by excessive high-shear rotation.

5. Acknowledgement

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